DTIC FILE COPY (2)

CONTRACT NUMBER N000014-85-C-0871

AD-A198 744

REPORT DOCUMENTATION PAGE

	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT This document has been approved for public release and sale; its distribution is unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report Number 4	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Microelectronics Center of North Carolina 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Defense Contract Administration Services Management Area - Atlanta
6c. ADDRESS (City, State, and ZIP Code) 3021 Cornwallis Road Research Triangle Park, N.C. 27709	7b. ADDRESS (City, State, and ZIP Code) 805 Walker St. Marietta, Georgia 30060-2789
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-85-C-0871
8c. ADDRESS (City, State, and ZIP Code) Dept. of the Navy 800 N. Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
THERMAL DECOMPOSITION OF COPPER BIS(HEXAFLUOROACETYLACETONATE)
(UNCLASSIFIED)

12. PERSONAL AUTHOR(S)
Reisman, Arnold (NCSU-MCNC); Temple, Dorota (NCSU)

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Tecnical Report # 4	FROM 8/1/87 TO 7/31/88	1988, July 28	9

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

See attached sheet

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL Pamela K. Adams	22b. TELEPHONE (Include Area Code) 919-248-1426 / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Thermal Decomposition of Copper Bis(hexafluoroacetylacetonate).

D. Temple, A.Reisman.[a)]

Microelectronics Center Of North Carolina.

P.O.Box 12889. Research Triangle Park, NC 27709

Abstract

Decomposition of the vapor phase of copper bis(hexafluoroacetylacetonate) under the effect of thermal activation was studied. It was found that the temperature at which the decomposition is carried out influences the chemical composition of deposits; the higher the temperature, the more carbon is incorporated. It is believed that this is the first time it has been demonstrated that metal-ligand decomposition in the copper compound has to be effected below the ligand decomposition temperature.

[a)]Also at Department of Electrical and Computer Engineering, Box 7911 North Carolina State University, Raleigh, NC 27695-7911

Introduction

Due to their high vapor pressures at temperatures below the decomposition range, metal hexafluoroacetylacetonates are well suited for use in chemical vapor deposition (CVD) processes. The CVD method is based on the decomposition of the vapor phase of a compound under the influence of some kind of energy (thermal activation, photon radiation,etc.) resulting in the deposition of a metal, alloy or compound in the form of a thin film.[1]

This report describes the results of a preliminary study on the thermal decomposition of metal hexafluoroacetylacetonates. Copper bis(hexafluoroacetylacetonate) ($Cu(hfa)_2$) was chosen as a model compound to investigate the influence of the process conditions on properties of the obtained deposits. Only a few attempts to obtain copper films by this method are reported in literature[2-4] and there is still a lack of data on the reproducible preparation of films with the required resistivity, for example.

Experimental

An experimental atmospheric pressure reactor was designed and constructed with the purpose of studying the thermal decomposition parameters of metal hexafluoroacetylacetonates. The apparatus consists of the following main parts (Fig.1):

-evaporator, **1** ,where the initial compound is evaporated,

-reaction chamber, **2** ,where substrates, **3** ,are placed and where the reaction of decomposition is carried out,

-diluent gas, **4** ,and carrier gas, **5**, manifold, exhaust and control system.

The susceptor, **6** ,in the reaction chamber is heated by means of high density radiant heater (model 5208; Research Inc.,P.O.Box 24064, Minneapolis,MN 55424) **7**. This type of heating makes it possible to avoid extensive heating of the reactor walls.

Copper bis(hexafluoroacetylacetonate) monohydrate (chemical formula $(CF_3\text{-}CO\text{-}CH\text{=}CO\text{-}CF_3)_2Cu*H_2O$) was purchased from Strem Chemicals, Inc. (7 Mulliken Way, Newburyport, MA 01950).

Thin film deposits obtained as a result of the thermal decomposition of copper bis(hexafluoroacetylacetonate) vapor phase were analysed by means of X-ray Photoelectron Spectroscopy (XPS), Rutherford Backscattering Spectroscopy (RBS) and X-ray Diffraction methods. The thickness of the films was measured by means of a stylus profilometer Alpha-Step model 200. Depositions were carried out on bare silicon wafers (i.e those with 1-2 nm of native oxide) and with oxidized wafers, with 200 nm of SiO_2. Argon (ultra-pure grade; Airco Industrial Gases, P.O.Box 12338, Research Triangle Park, NC 27709) was used as both the carrier and the diluent gas.

Results

A. Process Parameters.

In order to choose the optimum temperature to which the original compound should be heated, and the optimum flow rate of the carrier gas, we carried out a series of experiments: we determined the flow rate range which resulted in a constant reactant partial pressure reaching the reaction zone. The procedure (known as the transpiration method[5])was as follows: a known amount m_1 of $Cu(hfa)_2$ was placed in the evaporator which was heated to a chosen temperature. Then argon was allowed to flow(transpire) through the evaporation chamber for a certain time t after which the mass m_2 of the compound left in the evaporator was determined. Fig.2 shows the plot of $\frac{\Delta m}{V}$ vs. flow rate $F.R$ of the carrier gas ($\Delta m = m_1 - m_2; V = F.R. \times t$) for several temperatures of the evaporation zone. The plateau region corresponds to the conditions for which the gas medium in the evaporator is saturated with the vapor of the compound. In this region $\frac{\Delta m}{V}$ is proportional to the vapor pressure of the compound.

B. Influence of the Temperature of the Substrates On Film Composition.

Table 1 presents the results of the experiments performed in order to analyse the influence of the substrate temperature on chemical composition of the deposits. The chemical composition was determined by XPS and RBS methods. The temperature of the evaporator and the flow rate of the carrier gas were chosen, based on the data presented in Section A. The flow rate of the diluent gas was chosen so as to obtain an approximately uniform deposition along the susceptor.

The data presented in Table 1 indicate that the carbon content of the films increases with the temperature of the substrates. The low temperature (330°C) deposit consists of copper (no carbon, fluorine or oxygen were detected). The high temperature (650°C) product, however, is an amorphous carbon film, containing only isolated islands of copper, as determined from microscopic studies. This indicates that at low temperatures the reaction depicted by Eq.1

$$Metal-ligand \rightarrow Metal + Volatile Ligand \qquad (1)$$

dominates while at higher temperatures a reaction like that depicted in Eq.2

$$Metal-ligand \rightarrow Carbon + Volatile Metal-Ligand Fragment \qquad (2)$$

is competing with Eq.1 and dominates it.

Thicknesses of the films were in the range of 0.1 μm to 3 μm depending on the time of the deposition process and the temperature of the substrates. At 330°C under the conditions specified in Table 1 for obtaining pure copper deposits the film growth rate was of order of 2 nm/min.

The data in Table 1 indicate also that there is a threshold value of temperature below which no deposit of any kind was obtained.

Table 1. Chemical composition of deposits for different process conditions

(nd = not detected).

Run No.	Carrier Gas F.R. [ml/min]	Diluent Gas F.R. [ml/min]	Temp. of Evaporator [°C]	Temp. of Substrates [°C]	Composition of Deposits Percent by Weight			
					Cu	C	O	F
9	12	300	120	650	nd	100	nd	nd
5	12	300	120	500	3	88	9	nd
8	12	300	120	420	30	40	30	nd
11	12	300	120	330	100	nd	nd	nd
13	12	300	120	230	No Deposition			

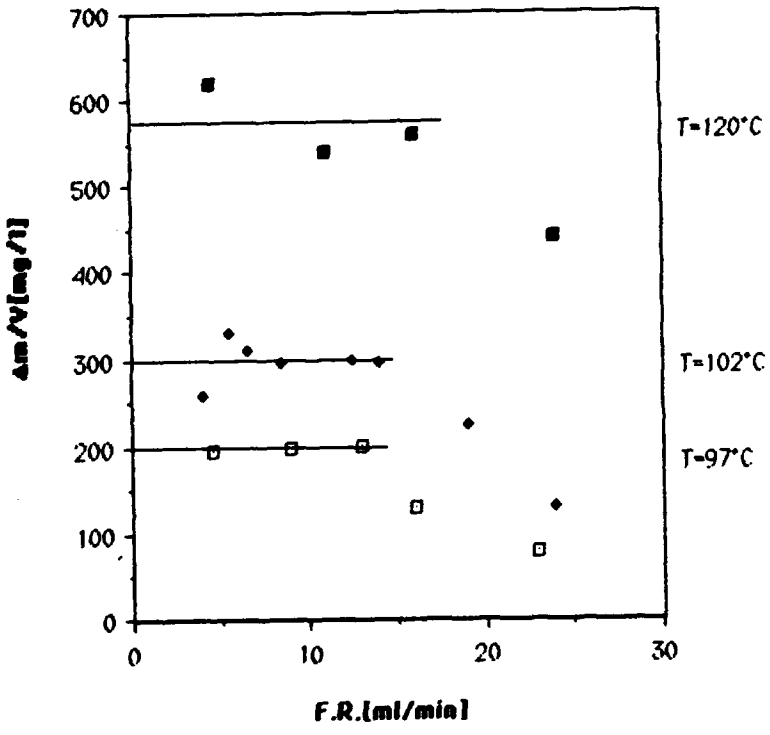

FIG.2. Plot of Δm/V vs. flow rate of argon.

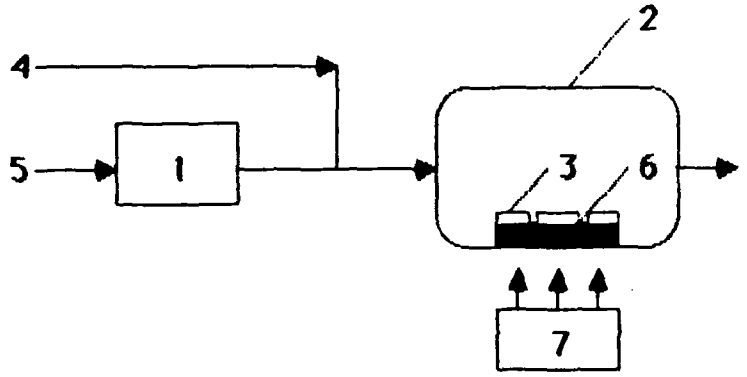

FIG. 1. Schematic representation of the CVD apparatus.
1-evaporator, 2-reaction chamber, 3-substrates,
4-diluent gas, 5-carrier gas, 6-susceptor and
7-radiant heater.

References

1. L.A.Ryabova, Current Topics in Materials Science **7**, 587 (1981).

2. F.A. Houle, C.R. Jones, T. Baum, C. Pico and C.A. Kovac, Appl. Phys. Lett. **46**, 204 (1985).

3. R.L.Van Hemert, L.B.Spendlove and R.E.Sievers, J.Electrochem.Soc. **112**, 1123 (1965).

4. R.W.Moshier,R.E.Sievers and L.B.Spendlove, U.S.Patent 3 356 527, (Dec. 1967).

5. A. Reisman, M. Berkenblit and S.A. Alyanakyan, J. Electrochem. Soc. **112**, 241 (1965).

Conclusions

Results of the preliminary studies on the thermal decomposition of copper bis(hexafluoroacetylacetonate) in an inert atmosphere of argon indicate that the substrate temperature is critical if pure copper film deposits are desired. The studies lead to the conclusion that at lower temperatures the reaction that dominates is one in which only Cu-O bonds in the metal-organic compound are broken and the ligands are volatilized with minimal fragmentation; thus, pure metallic films result. At higher temperatures the films contain carbon in addition to the pure copper because the organic ligand is also fragmented depositing carbon in the process. This carbon is incorporated in the growing film. The pure copper films were obtained for the substrate temperature equal to 330°C. The exact range is being investigated.

Subsequent studies will be carried out in order to determine the influence of other CVD parameters on film formation characteristics.

Acknowledgements

This work was supported in part by the Office of Naval Research.